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(54) Title: PURIFICATION OF PENTAFLUOROETHANE

(57) Abstract

A process for the purification of pentafluoroethane by removing chloropentafluoroethane therefrom which comprises contacting the impure pentafluoroethane in the gas phase with a liquid, polar organic compound extractant, preferably by countercurrent flow through a column, to form a liquid phase containing pentafluoroethane and recovering essentially pure pentafluoroethane from the liquid phase, preferably by simple distillation under reflux conditions. The liquid, polar organic compound may be an oxygen- and/or nitrogen-containing compound or a halogenated hydrocarbon.

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PURIFICATION OF PENTAFLUOROETHANE

This invention relates to a process for the purification of pentafluoroethane (HFC 125) and particularly to a process for removing chloropentafluoroethane (CFC 115) from mixtures of HFC 125 and CFC 115 to provide essentially pure pentafluoroethane.

It has been proposed to manufacture HFC 125 by hydrogenation of CFC 115 in the gas phase at elevated temperature in the presence of a hydrogenation catalyst or by hydrofluorination of perchloroethylene or dichloro-1,1,1-trifluoroethane (HCFC 123) over a fluorination catalyst. These and other processes result in HFC 125 containing impurities and in particular the impurity CFC 115 which may be present in an amount of up to 20% or more and which needs to be removed from HFC 125 which is to be used as or as a component of refrigerant compositions.

Removal of CFC 115 from HFC 125 is difficult in practice owing to the closeness of the boiling points of the components and the azeotrope or azeotrope-like composition which forms between them which renders complete separation by simple distillation impractical. At atmospheric pressure, CFC 115 boils at -38.7°C, HFC 125 at -48°C and the azeotrope at -55°C. At atmospheric pressure the azeotropic composition between HFC 125 and CFC 115 is about 85 mole% HFC 125: 15 mole% CFC 115 so that separation of HFC 125 and CFC 115 by azeotropic distillation entails significant loss of HFC 125 per mole of CFC 115 removed from the mixture. At higher pressure the relative volatility of HFC 125 opposite CFC 115 is close to 1.0 as 100% purity of HFC 125 is approached. This renders separation by simply distillation impractical or indeed impossible.

We have now found that a variety of organic compounds are able to extract HFC 125 preferentially from mixtures with CFC 115 and can be used to recover essentially pure HFC 125 from such mixtures.

According to the present invention there is provided a process for the purification of pentafluoroethane by removing chloropentafluoroethane therefrom which comprises contacting the impure pentafluoroethane in the gas phase with a liquid, polar organic compound selected from oxygen- and/or nitrogen-containing compounds and halogenated hydrocarbons to form a liquid phase enriched in pentafluoroethane and a gas phase depleted in pentafluoroethane, separating the liquid phase containing pentafluoroethane from the gas phase and recovering essentially pure pentafluoroethane from the liquid phase.

The organic compound preferably has a boiling point at least 20°C higher than the boiling point of pentafluoroethane so that recovery of pentafluoroethane from the liquid phase can be effected by simple distillation under reflux conditions at a pressure of up to 15 barg to remove pentafluoroethane as a gaseous top stream for collection and the organic compound as a liquid bottom stream which can be re-used in the treatment of impure pentafluoroethane.

Preferably in a continuous process the organic compound is recycled to the extraction stage of the process.

The organic compound, hereinafter referred to as the extractant is liquid under the conditions of use and is polar. Compounds of high polarity are preferred and in particular compounds having dipole moments in excess of 1 Debye, preferably greater than 1.5 and especially preferably greater than 2 Debye.

A wide variety of oxygen and/or nitrogen containing compounds may be used as the extractant, including saturated and unsaturated aliphatic compounds and aromatic compounds. The aliphatic compound may be straight-chain or branched-chain and it may be cyclic or acyclic. Examples of suitable compounds of this type include alcohols, aldehydes, ketones, nitriles, acids, acid anhydrides, furans, ethers, esters and compounds of mixed functionality such as partially fluorinated ethers. Mixtures of organic compounds may be used if desired. Examples of specific extractants of this type are acetone, methyl isobutyl ketone [MIBK], tetrahydrofuran, propionaldehyde, acetonitrile, diethyl ether and ethanoic anhydride. The boiling point of the extractant may vary over a wide range providing the extractant is liquid under the conditions of use. Compounds of boiling point above 100°C may be used. Any halogenated hydrocarbon can be used as the extractant which is liquid and polar and selectively dissolves pentafluoroethane from the mixture being treated. Usually the compound will contain at least two fluorine atoms, preferably at least three fluorine atoms and may contain one or more halogen atoms other than fluorine, notably chlorine atoms. Especially preferred are hydrofluorocarbons and hydrochlorofluorocarbons containing 2 to 4 carbon atoms. An example of a suitable hydrofluorocarbon is 1,1,2-trifluoroethane (HFC 143). An example of a suitable compound of mixed functionality is bis(fluoromethyl) ether.

Mixtures of extractants may be used if desired.

The extraction stage of the process may be carried out by passing the gaseous mixture over or through the liquid extractant but we prefer to pass the gaseous phase and the liquid in countercurrent through a column. In particular, we prefer to pass the gaseous phase upwardly through a column down which is flowing the liquid phase. We have found that operating in this way results in almost complete extraction of the pentafluoroethane into the liquid phase. Complete extraction of the pentafluoroethane in a single pass is not essential however, since if the extraction is incomplete so that the gaseous CFC 115 still contains pentafluoroethane, the CFC 115 can be recycled to the extraction stage of the process.

The extraction stage can be carried out at any temperature up to the boiling point of the liquid extractant. Room temperature can be conveniently used providing the extractant is liquid at this temperature. The pressure may be atmospheric, subatmospheric or superatmospheric pressure, the latter being preferred. Pressures up to 20 barg are useable although we prefer pressures below about 10-12 barg.

The amount of the extractant used preferably should be sufficient to extract substantially all of the pentafluoroethane from the mixture in a single pass through the column and is dependent upon the efficiency of the extraction. Usually an excess of the extractant will be used, typically a molar ratio of extractant: pentafluoroethane in the range 3:1 to 100:1.

A process according to the invention is illustrated in Figure 1 of the accompanying drawings which shows a flow sheet for a continuous process for the purification of pentafluoroethane. Referring to Figure 1, a gaseous stream 1 comprising a mixture of HFC 125 and CFC 115 is fed to the middle portion of a distillation column 2 into the top portion of which is fed a liquid extractant such as acetone, stream 3. The gaseous feed flows upwardly through the column countercurrent to the liquid extractant and HFC 125 is extracted from the gas into the liquid. CFC 115 is withdrawn from the top of the column, stream 4, and the liquid extractant now containing pentafluoroethane is withdrawn from the bottom of the column, stream 5. The liquid stream 5 containing pentafluoroethane is fed to the middle portion of a second distillation column 6 in which the liquid is distilled under reflux conditions to boil off the entrained pentafluoroethane which is removed from the top of the column as stream 7 and collected. The liquid extractant stream 8 withdrawn from the bottom of the column 6 is recycled as stream 3

to the top of the first distillation column 2 for re-use to extract pentafluoroethane from the feed stream 1.

The process according to the invention is useful for the treatment of any mixture of pentafluoroethane and CFC 115 to recover the pentafluoroethane in essentially pure form. The process is particularly useful for treating the product stream obtained during the manufacture of pentafluoroethane. Such a product stream typically contains other impurities in addition to CFC 115 and it will usually be treated to remove some at least of such other impurities before it is treated according to the present invention. Thus, for example, the product stream may be treated to remove hydrogen chloride and hydrogen fluoride (eg scrubbed with water or sodium hydroxide solution to remove hydrogen chloride and hydrogen fluoride), dried, distilled to remove low-boiling compounds and further distilled to separate the pentafluoroethane/CFC115 mixture from high-boiling compounds before the pentafluoroethane/CFC 115 mixture is treated with the extractant. A flow sheet for a process including these pre-treatments is shown in Figure 2.

Referring to Figure 2, the product stream 9 from the gas phase hydrofluorination of perchloroethylene to produce pentafluoroethane, after crude separation of the main recycle stream and scrubbing to remove hydrogen fluoride and hydrogen chloride and drying, is fed to the middle portion of a distillation column 10 from which a fraction 11 comprising low-boiling compounds or lights is withdrawn at the top and the remainder 12 containing high-boiling compounds or heavies is withdrawn from the bottom. The stream 12 is fed to the top portion of a distillation column 13 from which the heavies 14 are withdrawn at the bottom and a mixture 15 of pentafluoroethane and CFC 115 is withdrawn from the top. The mixture 15 is then fed as stream 1 to the process shown in Figure 1.

The invention is further illustrated but in no way limited by the following examples.

Examples 1-12

A vapour mixture of CFC 115 (1 ml) and HFC 125 (9 ml) were added to an evacuated 100 ml round-bottom flask fitted with a tap, a septum and a magnetic stirrer. The flask was returned to atmospheric pressure by addition of air and an additional 13 ml of air was added to create a slight positive pressure in the flask. A sample (5 ml) of the vapours in the flask was removed and analysed by gas chromatography to determine the initial composition of the mixture of HFC 125 and CFC 115. This procedure was

repeated 16 times; the average of the results gave an initial composition of the mixture of 12.4 mole% CFC 115 and 87.49 mole% HFC 125. The range of HFC 125 contents was from 86.18 mole% to 87.56 mole%.

The above procedure was then repeated except that a candidate extractant (10 ml liquid phase) was added to the flask before the gases were introduced. The liquid was stirred for 1 hour after introduction of the gases and then a headspace sample (5 ml) was removed for analysis by gas chromatography. Two runs (four runs in the case of acetone) were carried out on each extractant and the results are quoted in Table 1.

TABLE 1

Example No	Solvent	Headspace Composition (Mol%)		CFC 115 Enrichment Ratio*	Dipole** Moment (Debye)	Boiling Point (°C)
		CFC 115	HFC 125			
1	Acetone	24.7	75.3	1.98	2.88	56.2
		25.9	74.0	2.08		
		26.3	73.7	2.11		
		26.4	73.6	2.12		
2	95% Acetone/Water	21.5	78.5	1.73		
		22.6	77.4	1.81		
3	Ethyl Acetate	21.8	78.2	1.75	1.78	76
		24.3	75.8	1.95		
4	Propionaldehyde	23.9	76.0	1.92	2.52	48
		21.9	78.1	1.76		
5	Acetonitrile	22.2	77.8	1.78	3.92	81
		22.6	77.4	1.82		
6	Methyl isobutyl ketone	20.7	79.3	1.66	2.70	117
		18.6	81.4	1.49		
7	Tetrahydrofuran	17.9	82.0	1.44	1.63	67
		21.1	78.9	1.69		
8	Acetic Anhydride	18.4	81.6	1.48	2.80	139
		18.7	81.3	1.50		
9	Ethanol	16.7	83.4	1.34	1.69	78
		18.7	81.3	1.50		
10	Acetic acid	17.4	82.5	1.39	1.74	117
		13.2	86.8	1.06		
11	Diethyl ether	18.5	81.5	1.49	1.15	34.6
		14.7	85.3	1.18		
12	Triethylamine	16.2	83.8	1.30	0.66	88.8
		17.4	82.6	1.40		

* CFC 115 enrichment is calculated from the following ratio of mol% compositions

$$\left[\frac{[115]}{[115+125]}\right]\text{ headspace, final} \div \left[\frac{[115]}{[115+125]}\right]\text{ headspace, initial}$$

[ie solvents with a 115 enrichment ratio >1 preferentially dissolve 125]

**Data from (1) Handbook of Chemistry and Physics, 70th Edition, CRC Press, 1989
(2) Data Compilation Tables of Properties of Pure Compounds, Design Institute for Physical Property Data, American Institute of Chemical Engineering, 1984.

Examples 13-17

An evacuated 150 ml flask fitted with a tap, a septum and a magnetic stirring bar was charged with known vapour volumes of CFC 115 or HFC 125, and let back up to atmospheric pressure. An additional 20 mls of air was added to generate a slight positive pressure in the flask. A 5 ml vapour sample was removed and analysed by gas chromatography to confirm the initial vapour concentration of the fluorocarbon. A known liquid volume of solvent (5-20 mls) was added and the mixture stirred at 22°C for 30 minutes after which a further 5 ml sample was removed from the headspace and analysed by Gas Chromatography. The solubility of the fluorocarbon (and the partial pressure of fluorocarbon at equilibrium) was calculated from the difference in the initial vapour concentration of fluorocarbon and the concentration in the headspace after equilibration.

The results are summarised in Table 2 below, where α is the ratio of the concentration of dissolved HFC 125: concentration of dissolved CFC 115 at an equilibrium partial pressure of 0.4 atmospheres of fluorocarbon (ie HFC 125 or CFC 115) in the headspace.

TABLE 2

Example No	Solvent	α	Solubility (1)	Solubility (2)	Dipole Moment (Debye)	Boiling Point (°C)
13	Methyl isobutyl ketone (MIBK)	51	0.07	3.6	2.7	117
14	2,4-dimethyl-3-pentanone	6	0.6	3.7	2.7	124
15	3-pentanone	57	0.06	3.4	2.7	101.7
16	Acetonitrile	3.7	0.3	1.1	3.92	81
17	Acetone	2.3	3.5	8.1	2.88	56.2

Solubility (1) = Solubility of CFC 115 in mole fraction x 10^{-2}.

Solubility (2) = Solubility of HFC 125 in mole fraction x 10^{-2}.

From these results it is clear that HFC 125 is significantly more soluble than CFC 115 in these solvents.

Example 18

A vapour mixture of 70 mls HFC 125 and 70 mls CFC 115 was added to an evacuated 160 ml flask. The flask was let up to atmospheric pressure and then an additional 20 mls of air was added to generate a slight positive pressure in the flask. A 5 ml vapour sample was removed and analysed by gas chromatography to determine the initial vapour concentration of the fluorocarbons. 5 mls of liquid bis(fluoromethyl) ether [BFME] was added and the mixture was stirred at 0°C for 30 minutes after which time a 5 ml sample was removed from the headspace and analysed by Gas Chromatography to determine the final vapour concentration.

Two runs were carried out and the results are shown below.

Run 1

		% GC Area Counts
Initial vapour composition:	CFC 115	50.4
	HFC 125	49.6
Final vapour composition	CFC 115	60.1
	HFC 125	39.9

Run 2

		% GC Area Counts
Initial vapour composition:	CFC 115	49.3
	HFC 125	50.7
Final vapour composition	CFC 115	60.9
	HFC 125	39.1

From these results it is clear that HFC 125 is significantly more soluble than CFC 115 in BFME.

Example 19

A 150 ml Whitey bomb, fitted with a valve and septum, was evacuated and charged with 70 ml of HFC 125 and 70 ml of CFC 115. The bomb was let up to atmospheric pressure and a further 20 ml of air was added to put the bomb under positive pressure. A 5 ml sample of the head space was taken and analysed by Gas Chromatography. 6 gm of HFC 143 was then added and the Whitey bomb was left to equilibrate at ambient temperature for 30 minutes with agitation. After this time another 5 ml sample of the headspace was taken and analysed using Gas Chromatography. The results are given below.

		% GC Area Counts*
Initial Vapour Composition:	CFC 115	49.7
	HFC 125	50.3
Final Vapour Composition:	CFC 115	55.7
	HFC 125	44.3

*Discounting contribution from HFC 143

CLAIMS

1. A process for the purification of pentafluoroethane by removing chloropentafluoroethane therefrom which comprises contacting the impure pentafluoroethane in the gas phase with a liquid, polar organic compound selected from oxygen- and/or nitrogen-containing compounds and halogenated hydrocarbons to form a liquid phase containing pentafluoroethane and a gas phase depleted in pentafluoroethane, separating the resulting liquid phase from the gas phase and recovering essentially pure pentafluoroethane from the liquid phase.

2. A process as claimed in claim 1 wherein the liquid, polar organic compound is an oxygen- and/or nitrogen-containing compound.

3. A process as claimed in claim 1 or claim 2 wherein the impure pentafluoroethane in the gas phase and the liquid, polar organic compound are contacted by passing them in countercurrent through a column.

4. A process as claimed in any one of claims 1, 2 and 3 wherein the gas phase and the liquid phase are contacted at superatmospheric pressure up to 20 barg.

5. A process as claimed in any one of the preceding claims wherein the amount of the liquid, polar organic compound is such that the molar ratio of the organic compound: pentafluoroethane is from 3:1 to 100:1.

6. A process as claimed in any one of the preceding claims wherein recovery of essentially pure pentafluoroethane from the liquid phase is effected by distillation.

7. A process as claimed in claim 6 wherein the distillation is effected at a superatmospheric pressure up to 15 barg.

8. A process as claimed in claim 6 or claim 7 wherein the distillation is effected under conditions of reflux.

9. A process as claimed in any one of the preceding claims wherein the liquid phase, after recovery of pentafluoroethane therefrom, is recycled for use in treating impure pentafluoroethane.

10. A process as claimed in any one of the preceding claims wherein the liquid, polar organic compound has a dipole moment greater than 1 Debye.

11. A process as claimed in any one of the preceding claims wherein the liquid, polar organic compound has a boiling point of greater than 100°C.

12. A process as claimed in any one of the preceding claims wherein the liquid, polar organic compound is an aliphatic compound.

Fig.1.

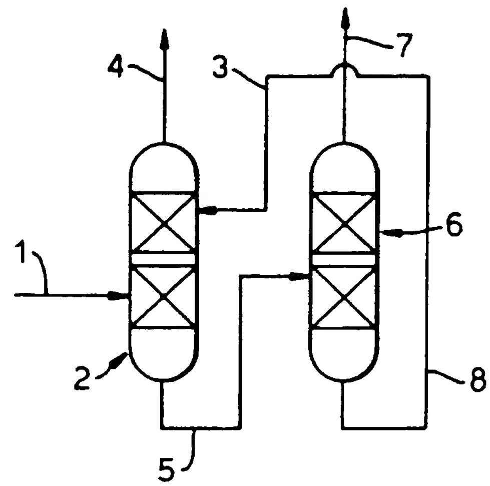
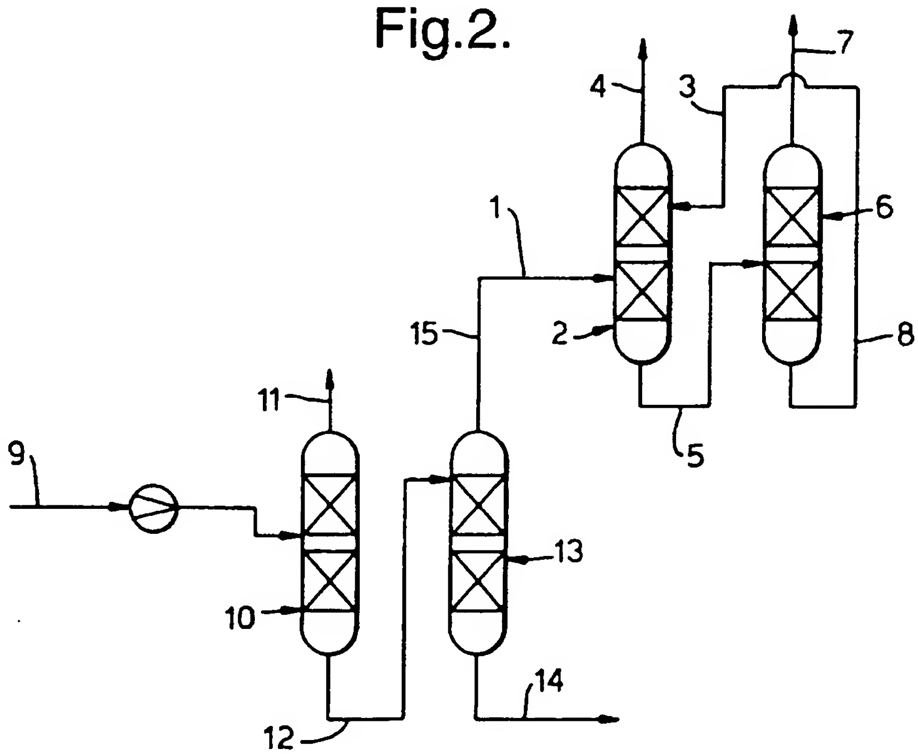


Fig.2.



INTERNATIONAL SEARCH REPORT

Interna l Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C17/38 C07C19/08 C07C19/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,B,14 68 451 (ONODA CEMENT COMPANY LTD.) 15 January 1970 see the whole document	1
A	US,A,5 087 329 (V.M. FELIX) 11 February 1992 see the whole document	1
P,A	EP,A,0 626 362 (SHOWA DENKO KABUSHIKI KAISHA) 30 November 1994 see the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
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Information on patent family members

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